Contaminant Flux and Fate in Fractured Rock

ESTCP Project ER-201570

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# Contaminant Flux and Fate in Fractured Bedrock

## Abstract

The objectives of this presentation are to:

- Identifying and characterizing DNAPL in bedrock
  - Edwards Air Force Base (AFB)
- Abiotic Dechlorination in Rock Matrices (coupled diffusion & reaction)
- Insights at Loring AFB

## Subject Terms

Contaminant Flux and Fate, Fractured Bedrock
**Contaminant Flux and Fate in Fractured Rock**

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October 27, 2016
Well established tools and insights in overburden

Lack of tools and insight in bedrock
Chlorinated Solvents in

What is sustaining Perchloroethylene (PCE)/Trichloroethylene (TCE) plumes in bedrock?

- Dense non-aqueous phase liquid (DNAPL)?
- Matrix back-diffusion?
- Low permeability fractures?
- Overburden impact?

How quickly is contaminant mass attenuating?

Objectives

- Identifying and characterizing DNAPL in bedrock
  - Edwards Air Force Base (AFB)

- Abiotic Dechlorination in Rock Matrices
  (coupled diffusion & reaction)

- Insights at Loring AFB
1. DNAPL ARCHITECTURE & DISSOLUTION

The DNAPL Challenge
- Most of the contaminant mass may be in the non-aqueous phase
- Dissolution rate may limit remedial effectiveness and mass discharge
- Locating and contacting DNAPL sources can be challenging

Complicating Factors in Bedrock
- Many of the technologies for locating and quantifying DNAPL sources are not appropriate, or have not been demonstrated, for bedrock
- DNAPL may be even more difficult to contact in fractured bedrock
- Costs
Illustrative Example – Key Insights

Site 37 Characteristics
- Large plume (390 acres)
- Deep (>200 feet)
- Granite bedrock (quartz/feldspar)
- Low transmissivity
- Fracture flow
- PCE at >10% solubility
- No direct evidence of DNAPL (prior to this project)

Demonstration Location - Edwards AFB
(ESTCP 201210)
~100 mL/min recirculation flow
Borehole geophysics

Discrete interval sampling and short-term pump testing

18 PCE concentrations
Partitioning Tracer Testing (PTT)

Applicable to Unconsolidated and Consolidated Materials

Compare elution of conservative and partitioning tracers (alcohols) to verify and quantify DNAPL

Annable et al., JEE, 1998
Tracer Results – Deep Zone

Bromide mass eluting through each zone proportional to transmissivity

Initial Peak (low T fracture)
- 1% of flow
- Sn = 0.007

Middle Peak
- 9% of flow
- Sn = 0.0

Late Peak
- 40% of flow
- Sn = 0.0004

Mass transfer-controlled tailing
What Else Does This Tell Us?

**DNAPL distribution**
DNAPL present in high transmissivity fractures, but also in low transmissivity zones

**Average fracture porosity**
0.004

**DNAPL mass**
2.4 kg in 15 ft radius around injection well interval

**DNAPL persistence under ambient conditions (dissolution only)**
B11s (high T) – 65 years B11d (tail) – 13 years
B11d (low T) – 194 years
PCE Mass Distribution and Flux

Rock Matrix vs Fractures

Based on PTT DNAPL

149 g PCE in rock matrix

PCE concentration profile suggests back-diffusion not occurring

Treating to remove DNAPL might make sense

2,400 g PCE as DNAPL in fractures
Bioaugmentation Results

Substantial chloride generation indicated DNAPL dissolution (2.1 mM of PCE to Dichloroethylene [DCE])

Chlorinated volatile organic compounds (CVOC) & ethene are not the best indicator of DNAPL removal (Schaefer et al. ES&T, 2010)
Impacts of DNAPL Architecture on Treatment During Bioaugmentation

- B11S
  - Relative Concentration ($C/C_0$)
  - Time Elapsed (days)
  - 24DMP
  - Bromide

- B11D
  - Relative Concentration ($C/C_0$)
  - Time Elapsed (days)
  - 24DMP
  - Bromide

~100% DNAPL removal
Limited rebound (97% CVOC decrease)
High DNAPL diss. enhancement

Only 45% DNAPL removal
Rebound
Low DNAPL diss. enhancement

**But a small fraction of DNAPL mass removal may result in a large improvement in groundwater**
2. Rock Matrix Dechlorination Reactions

- Matrix diffusion is a SLOW process, so even a slow dechlorination reaction can be significant.

- Several studies have focused on abiotic dechlorination reactions facilitated by naturally occurring ferrous minerals:
  - Bedrock matrices have received little attention
  - Ferrous minerals are present in many bedrock aquifers

- Are such reactions occurring, can they be measured, and are they important for my site?
Rock Core Collection (SERDP Project ER-1685)
former Naval Air Warfare Center, Trenton, NJ

Lockatong Formation:
- Multiple types of mudstones and shale
- Multiple water bearing fractures
- Ferrous iron minerals

Stockton Formation
- Multiple water bearing fractures
- Red and white sandstones/siltstones

Cores collected outside of the TCE plume
Diffusion Cell Experiments

Iodide tracer experiments to assess diffusion parallel and normal to bedding - four rock types
### Iodide Diffusion Results: Impact of Mineral Bedding

#### SEM Images

<table>
<thead>
<tr>
<th>Material</th>
<th>SEM Porosity (Normal)</th>
<th>SEM Porosity (Parallel)</th>
<th>Effective Diffusion Coefficient (cm²/s) Normal</th>
<th>Effective Diffusion Coefficient (cm²/s) Parallel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Sandstone</td>
<td>0.074</td>
<td>0.069</td>
<td>1.8 x 10⁻⁷</td>
<td>2.3 x 10⁻⁷</td>
</tr>
<tr>
<td>Tan Sandstone</td>
<td>0.068</td>
<td>0.085</td>
<td>1.3 x 10⁻⁷</td>
<td>1.9 x 10⁻⁷</td>
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<tr>
<td>D.G. Mudstone</td>
<td>0.050</td>
<td>0.11</td>
<td>0.49 x 10⁻⁷</td>
<td>2.8 x 10⁻⁷</td>
</tr>
<tr>
<td>Quarry Sandstone</td>
<td>0.085</td>
<td>0.037</td>
<td>6.5 x 10⁻⁷</td>
<td>0.68 x 10⁻⁷</td>
</tr>
</tbody>
</table>
Predicting Diffusion Based on Apparent Porosity

\[
\frac{D_{\text{eff}}}{D_{\text{aq}}} = \varepsilon^{2.2}
\]

(Boving and Grathwohl, 2001)
Coupled TCE Diffusion and Reaction

Light Gray Mudstone

TCE

\[ \frac{C}{C_0} \]

Measured Flux

TCE Source

Acetylene + Ethene + Ethane

\[ \frac{C}{C_0} \]

Degradation Products

\[ \frac{C}{C_0} \]

Days

HgCl\textsubscript{2} added to inhibit microbial activity
Available Ferrous Iron

SEM for porosity distribution

Electron Dispersive Spectroscopy for Fe\textsuperscript{2+} distribution

“Available” Fe\textsuperscript{2+} indicated by blue
Coupled Diffusion and Reaction of TCE through Rock
- Up to 10 months exposure at elevated TCE concentrations (200 mg/L) did not result in any decrease in the observed dechlorination rate constant

- Low stoichiometric Fe$^{2+}$ consumption (<2%)

But are these reactions really occurring in historically contaminated bedrock aquifers?
Collect Core from within the TCE Plume

- Collection at the former Naval Air Warfare Center, Trenton, NJ, USA

- Core collected adjacent to fractures at three depth intervals
Groundwater Data as Screening for Potential Abiotic Dechlorination Reactions

### Groundwater Packer Sampling (µg/L)

<table>
<thead>
<tr>
<th>Compound</th>
<th>49'</th>
<th>53'</th>
<th>83'</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>203</td>
<td>463</td>
<td>24,800</td>
</tr>
<tr>
<td>cis-DCE</td>
<td>59</td>
<td>410</td>
<td>260</td>
</tr>
<tr>
<td>vinyl chloride</td>
<td>2</td>
<td>31</td>
<td>6.2</td>
</tr>
<tr>
<td>methane</td>
<td>28</td>
<td>31</td>
<td>4.8</td>
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<tr>
<td>ethane</td>
<td>3.2</td>
<td>2.0</td>
<td>0.48</td>
</tr>
<tr>
<td>ethene</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>propane</td>
<td>2.4</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td>acetylene</td>
<td>-</td>
<td>-</td>
<td>4.8</td>
</tr>
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Abiotic TCE Dechlorination in Rock Collected within the TCE Plume

Comparison of TCE spiked vs. non TCE spiked samples in laboratory system

Rock minerals still able to dechlorinate TCE (similar rate constant)
How Important are These Reactions?

Simulated 30 years of uptake

Dechlorination half-life = 2.1 years
How Important are the Reactions?

Diffusion Simulations
- After 30 years constant TCE exposure, 30 years of back-diffusion (maximum gradient: no TCE in fractures)

Can help determine if matrix back-diffusion is sustaining the plume
More Evidence

PCE/TCE concentrations profiles in the rock matrix moving inward from the fracture interface (cm-scale):

- **Loring AFB Limestone**
  - Batch testing showed substantial abiotic reactivity

- **Edwards AFB Granite**
  - Batch testing showed negligible abiotic reactivity
How Readily Can This Information Be Attained?

Initial Screening

- Porosity analysis
  - <$400/sample Several commercial labs

- Reduced gases in groundwater (acetylene, propane, ethane, ethene)
  - <$100/sample Several commercial labs (ask for gases)

- Ferrous iron in crushed rock (EPA Method SM3500-Fe B.4.c)
  - ~$75/sample ALS Environmental & McCampbell Analytical

Next Steps - Using Intact Rock Core:

- Field crushing and methanol extraction of rock “slices”
  - $10K (not including drilling) Several labs

- Batch reactivity and sorption testing
  - ~$25K lab cost (assuming core available) Published methods
3. Impacts of Matrix Diffusion and Reaction on the Dissolved Plume: Loring AFB – Groundwater Management Zone (GMZ) 4

**GMZ 4**
- fractured limestone
- complex fracture flow
- former drum disposal
- PCE (DNAPL likely)
- prior steam injection
- no groundwater data for ~10 years

Remedial efforts as part of sitewide performance based contract (CB&I)

USAF, Maine DEP and USEPA very involved
PCE Source Area in Fractured Limestone
Identify High Contaminant Flux Zones

QBC1 EX3

EX2

EX1

EX4 VEA5

[Map with identified zones and flux values]

- 6.4 x 10^{-2}
- 2.1 x 10^{-2}
- 7.8 x 10^{-4}
- 2.9 x 10^{-3}
Target Treatment Area
Bioaugmentation to Target High PCE Flux Zone

Treatment is on-going
Preliminary Assessment – Role of Matrix Dechlorination Reactions

**Determine:**
- Fracture aperture (cubic law and transmissivity) \[0.021 \text{ cm}\]
- Superficial velocity (Darcy’s Law and fracture porosity) \[400 \text{ cm/day}\]
- Rock matrix effective diffusion coefficient estimated from rock matrix porosity \[3.6 \times 10^{-9} \text{ cm}^2/\text{s}\]
- First order dechlorination rate constant \[6.6 \times 10^{-7} \text{ s}^{-1}\]

Flux at fracture surface = 2 erf \[
\left[ \sqrt{\frac{t}{\pi \tau}} \right]
\]

(Crank, 1995)
Role of the Rock Matrix for Natural Attenuation of the Downgradient Dissolved Plume

Fractional Decrease in Mass Discharge

Feet downgradient

No reaction in matrix

With matrix reaction

Model assumes no dilution due to dispersion
Conclusions

• Residual DNAPL can be identified and quantified in fractured rock

• DNAPL in low transmissivity fracture zones may be sustaining bedrock plumes

• In DNAPL source areas, most of the contaminant mass and flux might be due to DNAPL
  - thus, treatment may be worthwhile

• Abiotic dechlorination reactions in rock matrices may be mitigating back-diffusion and contaminant migration at many sites

• Identifying and quantifying these dechlorination reactions can be readily performed
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